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(21) International Application Number: PCT/AU92/00220 (22) International Filing Date: 15 May 1992 (15.05.92) (30) Priority data: PK 6167 16 May 1991 (16.05.91) AU (71) Applicant (for all designated States except US): QUBATOR PTY LIMITED [AU/AU]; 14 Miramont Avenue, Lane Cove, NSW 2066 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : BRANSON, Robin [AU/AU]; 14 Miramont Avenue, Lane Cove, NSW 2066 (AU). VANCE, Eric, Raymond [AU/AU]; 21 Gorada Venue, Kirrawee, NSW 2232 (AU). (74) Agent: F.B. RICE & CO.; 28A Montague Street, Balmain, NSW 2041 (AU).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), LU (European patent), MC (European patent), NL (European patent), NO, RU, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: PROCESS FOR CONVERTING SPENT POT LINER (57) Abstract A process for rendering spent pot liner (SPL) to a state where it is environmentally non-hazardous and preferably commercially useful in which it is converted to a ceramic material by heat treatment with additives and wherein cyanides are converted to environmentally harmless species and fluorides are chemically bound into the ceramic material.		

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PROCESS FOR CONVERTING SPENT POT LINERTECHNICAL FIELD

The present invention relates to a process by which environmentally hazardous industrial waste material comprising predominantly but not exclusively spent pot liner (SPL) or similar waste material is combined with other substances to produce a ceramic material, of markedly reduced hazard to the environment, which preferably is manufactured into commercially valuable products but which at least constitutes a suitable medium for the permanent disposal of SPL. The invention will be described with particular reference to SPL, but it will be appreciated that it is not limited to solely processing that material.

SPL is produced from aluminium smelters as a waste product. It is heterogeneous, consisting typically of graphite, refractory, alumina, cryolite (a compound of fluorine), sodium cyanides, metallic iron and aluminium.

If water (for example as rain) comes into contact with SPL, cyanides and fluorides may be washed out of the SPL in the form of a leachate because of the solubility of both substances in water.

In some parts of the world, several Australian states among them, relevant environmental protection authorities (EPA's) have classified such leachates as toxic substances and are prohibiting the permanent disposal of SPL, particularly by land fill or burial, unless leachate concentration, typically measured in parts per million (ppm) of contaminant, is below a maximum level stipulated from time to time by the EPA.

BACKGROUND ART

Various proposals have been put forward for dealing with SPL as exemplified by US patents 4993323 and 4763585. The primary purpose of the invention of US 4993323 is to facilitate combustion of the SPL in a

fluidised bed at a higher temperature than was previously attainable without agglomeration. Secondary purposes are to pyrolyse the cyanides, create insoluble calcium fluorides and minimise HF off gas. It is claimed the
5 output is an ash which is non-hazardous. This objective is achieved by adding to the raw SPL, calcium (in the form of limestone) and lignite.

US Pat No. 4,763,585 deals specifically with the problem of agglomeration in fluidised bed combustion by
10 means of a physical coating over the sticky particles which cause the problem.

A principal purpose of this invention is to immobilise the toxic components of the hazardous waste (SPL) in a ceramic material. For example, the fluorides
15 contained in SPL are formed into a compound which is sufficiently insoluble in water to render the ceramic material containing the compound non-hazardous. The ceramic material is therefore a suitable medium for the permanent disposal of SPL. Another effect of the process
20 of this invention is that the cyanides contained in SPL are pyrolysed into harmless species.

The process of the invention may incorporate waste material from other manufacturing processes, such as dead burnt calcium sulphate but is not limited to doing so.

25 The process of the invention preferably produces materials which have a commercial value, independent of any value which may be attributed to the permanent disposal of SPL.

DISCLOSURE OF INVENTION

30 The present invention provides a process for the treatment of spent pot liner (SPL) or chemically similar material comprising:

crushing raw SPL to a size suitable for combustion;
combusting the crushed SPL material for a period and
35 at a temperature sufficient to pyrolyse cyanides in said

material into environmentally harmless species and to oxidise the graphite content of the material, thereby producing a substantially carbon free ash;

5 mixing and milling the ash with additives comprising chemically reactive compounds selected to immobilise fluorine and other materials required to produce a desired ceramic material;

10 heating the mixture for a sufficient period and at a temperature required to cause chemical combination of the reactive compounds in the mixture to produce a heat treated ceramic material.

By altering the proportions of SPL ash, and additives such as alumina, calcium or magnesium compounds and/or the addition of other compounds, ceramics may be produced by
15 the process of the present invention for a wide variety of applications including refractory lining, civil engineering construction, wear surfaces, industrial components and domestic ceramic artefacts.

If further processing is required to produce a
20 desired end product, the heat treated solids may be crushed, milled and screened to provide a suitable grog which is then mixed by conventional means with suitable additives such as binders, pressed into a final shape and sintered.

25 One example of the process of the present invention employed raw SPL crushed by conventional means and burnt in a muffle furnace to produce a substantially carbon free ash. The resultant SPL ash was mixed with additives, milled, pressed into briquettes and heated. The
30 briquettes were then crushed and screened to produce a grog with the fractions of different particle sizes required for optimum packing density when forming the final product.

The grog fractions were mixed in specified
35 proportions with a binder and water and pressed into

blocks and dried. The blocks were sintered in a muffle furnace.

BEST MODES

The particulars of an example of the present
5 invention will now be described by the following:-

ASH PREPARATION

Raw, untreated SPL was crushed to 2mm and spread evenly to a depth of 25mm on inconel trays measuring 1500mm by 700mm by 45mm. The trays were loaded 4 at a
10 time into a muffle furnace.

The furnace temperature was ramped to 600°C at a rate of 200°C/hour and held at this temperature for 32 hours. It may not have been necessary to combust the SPL for 32 hours but the combustion time was extended to
15 minimise the carbon content.

PREPARATION FOR HEAT TREATMENT

Additives:

Ad1 - Calcium Sulphate dead burnt at approximately 400°C.

20 Ad2 - Aluminium oxide heated at 800°C.

Procedure:

Two batches of mixture were prepared using the following formulae:

Batch 1: - 32.52% by wt SPL + 59.35% by wt Ad1 + 8.13% by wt Ad2

25 Batch 2: - 33.48% by wt SPL + 52.04% by wt Ad1 + 14.48% by wt Ad2

The SPL ash was mixed with the additives in a 900mm diameter Simpson mixer for 10 minutes.

Milling and Shaping

Each batch was milled separately using a 450mm
30 diameter hammer mill such that approximately 95% of the material passed through a 100 mesh screen ie. - 150 microns.

The milled mixture was pressed dry, without binders or other additives, into briquettes using a single roll
35 press applying approximately 15 tonnes

pressure/briquette. If all that is required is to produce a grog then it will not be necessary to form briquettes. It is believed good enough to feed the powder through a roll press to produce cake for heating.

5 Heat Treatment

The briquettes were piled approximately 100mm high onto the inconel trays mentioned above, which had been lined with Kao board approx. 20mm thick, and loaded into the muffle furnace.

- 10 The furnace was ramped at 300°C/hour to a temperature of 1050°C and held at this temperature for 2 hours.

Grog Preparation

- 15 The heat treated briquettes were crushed in a roll crusher, milled in the hammer mill mentioned above and screened to obtain the following fractions of different material sizes for each batch, as determined by a screen analysis:

- 20 42.86wt% - 4mm +2mm
9.52wt% - 0.5mm + 0.25mm
26.98wt% - 0.25mm + 0.063mm
20.63wt% - 0.063mm

25 Green Shaping

- Each batch was mixed with 2%wt dry Lignosol binder and tap water (equivalent to 4%wt of a 50/50 lignosol - tap water solution used in practice). The resulting mixtures were pressed into blocks measuring 235mm by 115mm
30 by 75mm each weighing approximately 5kg. The blocks were dried for 24 hours at 150°C.

Sintering

- The blocks were sintered in the same muffle furnace mentioned above using the following regime: ramp at
35 180°C/hour to the sinter temperature of 1150°C:

hold for 5 hours; cool at 300°C/hour.

Ancillary Processes

The broadest process of the invention produces a material which may be subjected to ancillary process to achieve additional useful results such as the improvement of the ceramic body and the retrieval of re-usable elements or compounds. One example is given:

Removal of Sodium by Leaching

Sodium in a ceramic may inhibit its use for certain purposes. This method of removing sodium from the calcined briquettes or sintered material is possible because the fluorides have been fixed so only sodium will come out in solution.

Sintered blocks from the aforementioned example were crushed and milled into a grog of different fractions as follows:

- Crush to yield 45wt% of total - 4 + 1mm
- Screen residue to yield 10 wt% - 1 + 0.25mm
- Mill residue to yield 30 wt% - 0.25 + 0.075mm
- Screen residue to yield 15 wt% - 0.075 + 0.025mm

The grog was leached for 24 hours in de-ionised water at the rate of 5lt/kg of material and then dried in preparation for further processing. Sodium may be recovered by conventional evaporation of the leachate.

In another example in accordance with the invention, samples of SPL crushed to an average particle size of 20mm were combusted in a muffle furnace at between 600-700°C and then milled to a powder.

The powder was mixed with calcium sulphate and alumina in the approximate proportions 30% by weight - SPL; 60% by weight - calcium sulphate; 10% by weight alumina and heat treated at 800°C at atmospheric pressure for 3 hours.

The formed shapes from the resulting heat treated mixture were sintered in air at atmospheric pressure at

1150°C for 1 hour using a heating rate of 3°C per minute to achieve the steady state temperature.

A sample of the resulting ceramic was subjected to a USA leach test, EPA TCLP (method 1311) which produced a
5 leachate containing 13ppm fluorides. (New South Wales (Australia) current permissible maximum is 150ppm).

In another example, calcium hydroxide was used in place of calcium sulphate in approximately the same proportion; the process being carried out under the same
10 conditions. Mechanical properties of the resulting ceramic appeared to be comparable to those obtained by using calcium sulphate. The same leach test produced a leachate containing 171ppm of fluorine.

In a further example of the invention 105 parts by wt
15 (grams) SPL ash were mixed with 78 parts by wt of calcium sulphate and 16 parts by wt of alumina. The mixture was formed into a tablet 50mm diameter by 25mm thick and heated in a muffle furnace at 1140°C for three hours.

In a still further example of the invention 45 parts
20 by wt (grams) of SPL ash were mixed with 195 parts by wt calcium sulphate and 32 parts by wt of alumina. The mixture was formed and heat treated as in the above further example.

As can be seen from these further examples the
25 invention can be readily operated with an SPL ash to additive ratio in the range of 1:1 to 1:5.

In operating examples of the present invention no additives are put with the raw SPL before it is combusted to an ash.

30 The raw SPL is combusted at a temperature of 600-800°C.

Two steps beyond the production of an ash are involved. (producing ash is almost incidental to the main process in that a substantially carbon free ash produced
35 by any method will suffice for the purposes of the

invention).

It appears that in the method of the present invention the sulphates act like a flux or catalyst in the process of fixing the fluorides. Sulphates, or a
5 substitute for them, are highly beneficial to the process.

Simple experimentation can determine the optimum proportions of calcium, sulphates, alumina and/or other additives to achieve a desired result. For example, clay was substituted for alumina in a mixture of SPL ash and
10 calcium sulphate corresponding to Batch 2. The mixture was pressed into briquettes which were heated at 1050°C for 2 hours. The resulting ceramic was similar to that produced by using alumina but with apparently useful distinguishing characteristics. It may, for example, be
15 possible to incorporate sodium into refractory aluminium sodium silicate which is conducive to producing a better quality ceramic.

A muffle furnace has been used to date for combusting the raw SPL whereas a rotating furnace may reduce the
20 residence time of the charge without having to substantially raise the temperature. The principal objective at the initial stage is to achieve a substantially carbon free ash. Subsequent heat treatment will remove any residual cyanides.

25 The present invention facilitates a complete disposal strategy for SPL and other similar hazardous materials. The output from the process must, therefore, be a product which does not depend exclusively for its disposal on being the input to another industrial process.

30 It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments
35 are, therefore, to be considered in all respects as illustrative and not restrictive.

CLAIMS:

1. A process for the treatment of spent pot liner (SPL) or chemically similar material comprising:
 - crushing raw SPL to a size suitable for combustion;
 - 5 combusting the crushed SPL material for a period and at a temperature sufficient to pyrolyse cyanides in said material into environmentally harmless species and to oxidise the graphite content of the material, thereby producing a substantially carbon free ash;
 - 10 mixing and milling the ash with additives comprising chemically reactive compounds selected to immobilise fluorine and other materials required to produce a desired ceramic material;
 - heating the mixture for a sufficient period and at a
 - 15 temperature required to cause chemical combination of the reactive compounds in the mixture to produce a heat treated ceramic material.
2. A process as claimed in claim 1 wherein the mixture is formed into discrete solid shapes prior to said heating.
- 20 3. A process as claimed in claim 1 or 2 wherein the spent pot liner material is combusted in a muffle furnace or a rotating furnace.
4. A process as claimed in any one of the preceding claims wherein the spent pot liner material is combusted
- 25 at 600-800°C.
5. A process as claimed in any one of the preceding claims wherein the ratio by weight of SPL ash to the additives is between 1:1 and 1:5.
6. A process as claimed in any one of the preceding
- 30 claims wherein the heat treated ceramic material is crushed, milled, screened, mixed in predetermined proportions with further additives, formed into shapes and sintered to a final ceramic product.
7. A process as claimed in any one of claims 1-5
- 35 comprising leaching sodium from the heat treated ceramic

material.

8. A process as claimed in claim 6 comprising leaching sodium from the final ceramic product.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION AND SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent classification (IPC) or to both National Classification and IPC
Int. Cl.⁸ B09B 3/00; C04B 35/64, 35/68.

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

IPC

B09B 3/00; C04B 35/64, 35/68

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched⁸

AU: IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
A,P	AU,A, 75394/91 (ALCAN AUSTRALIA LIMITED) 7 November 1991 (07.11.91) See whole document.	
A,P	US,A, 5,024,822 (HITTNER et al.) 18 June 1991 (18.06.91) See whole document.	
A	US,A, 4,956,158 (HITTNER et al.) 11 September 1990 (11.09.90) See whole document.	
A	EP,A, 117761 (ALCAN INTERNATIONAL LIMITED) 5 September 1984 (05.09.84) See whole document.	

^{*} Special categories of cited documents : ¹⁰

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document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
18 August 1992 (18.08.92)

Date of Mailing of this International Search Report

27 Aug 1992 (27.08.92)

International Searching Authority

AUSTRALIAN PATENT OFFICE

Signature of Authorized Officer

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/A/92/00220

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member		
US	5024822	US 4956158		
EP	117761	AU 25174/84	CA 1216008	ES 530160
		ES 8500772	JP 59171563	NO 4576651
		US 4576651		